

Mineral Ores as Disposable Catalysts in Coal Liquefaction

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INTRODUCTION

Coal constitutes the largest single fossil fuel resource in the U.S. Until the last few years, its use did not increase with increased fuel demands because of environmental restrictions and the ready availability of petroleum and natural gas. Now that the demand for liquid and gaseous fuels has surpassed the nation's capability to supply them without excessive imports, use of coal must increase both in power plants and as a means of producing petroleum and natural gas.

Reduced American reliance upon imported energy supplies hinges on the use of more domestic coal, through direct burning in the short-term, and through gasification and liquefaction in the long term. Although it is not yet economically feasible to convert coal into synthetic gasoline, jet fuel or diesel fuel oil, the technical feasibility of such a process has been proved. A number of liquefaction systems have been developed through the pilot plant stage, covering a wide range of alternative technologies.

However, there are a number of problems associated with the production of liquid fuels from coal -- loss of expensive catalyst, high pressure equipment, and environmental pollution -- that remain unsolved. But the basic problem is economic, mainly due to the high cost of hydrogen, high pressure equipment, and catalysts. Hydrocarbons, including natural gas, LPG, naphtha, etc., are the principal process raw materials for the manufacture of hydrogen these days. The high cost of these raw materials for the manufacture of hydrogen is one of the reasons for the synthetic liquid fuel from coal to be more expensive than natural crude oil (1). However, production of hydrogen from coal which is a proven technology will make the coal liquefaction more attractive. Secondly, by using highly active catalysts, hydrogenation pressure has been cut down to 2000 - 3000 psig (13,790-20,685 kPa) which would considerably reduce the cost of commercial reactors.

The greatest problem in the direct hydrogenation yet to be solved is the use of commercial catalysts which are expensive, with short life and cannot be recovered or regenerated. The answer to this problem is to find a low cost disposable catalyst(s). Our work and that of others have well established that cobalt and molybdenum are good catalysts for hydrogenation and hydrodesulfurization of coal, whereas nickel and molybdenum are effective for coal hydrodenitrogenation. The most inexpensive source of these metals is their ores where they are present mostly as sulfides or oxides. Use of these ores in coal liquefaction as disposable catalysts must be explored.

The object of this study was to investigate the hydrogenation of coal-SRC-11 oil slurry using disposable ore catalysts (DOC) at the SRC-11 process operating conditions with special reference to maximizing liquefaction and minimizing viscosity of the product oil. All experiments were conducted at 425°C and 2000 psig (13,790 kPa) hydrogen pressure for a period of half an hour.

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LITERATURE REVIEW

There is considerable published work on the various aspects of coal liquefaction. One of the authors of this paper has presented detailed literature reviews for coal hydrogenation and hydrodesulfurization in his papers (2,3).

Hydrodenitrogenation (HDN) is of interest and importance for the synthetic fuels industry for minimizing NO_x formation during the combustion of coal-derived oil. This oil contains unacceptably high levels of nitrogen. So far, nitrogen removal has not received nearly as much attention as has desulfurization because sulfur, a severe catalyst poison and a serious atmospheric pollutant, has historically been the primary concern in processing petroleum feedstocks. Research work on hydrodenitrogenation using hydrogen or syngas is limited (4,5,6,7,8,9).

Rationale for the Use of Ores as Catalysts: Coal liquefaction takes place through metal -- catalyzed reactions. It is also reported that metallic catalysts in general are not expected to survive as metals in a coal liquefaction environment at sulfur levels exceeding 1%. It has been shown that all metals can form bulk sulfides under these conditions, and therefore the true catalyst would be a mixed sulfide and not a bimetallic system (9). In the presence of hydrogen at 380-440°C and pressures between 2000-3000 psig, (13,790-20,685 kPa), the metallic oxides are expected to be reduced to metals or get converted to sulfides or oxysulfides. Further, it has been well demonstrated (10,11) that mineral matter, particularly pyrite, in coal acts as a catalyst during hydrogenation. Inclusion of these ores individually or as mixtures of various ores, providing Co, Mo, and Ni, etc. should catalyze hydrogenation, hydrodesulfurization, and hydrodenitrogenation of coal.

Some of these metals are present in their ores in low concentration and may have to be beneficiated to increase their content by removing the inert material. Concentrate containing cobalt four to eight times higher than that of the ore can be obtained by flotation technique alone (12,13). Other ore dressing techniques can also be used. Since the equipment and operation of ore dressing are relatively inexpensive, the cost of the upgraded ore will still be comparatively low.

Lastly, it may be possible to recover these metals from the waste unconverted coal-ash-DOC mixture or ash-DOC mixture (rejects from SRC-II gasifier) by conventional metallurgical processes making the use of these ores as catalysts all the more attractive.

OCCURRENCE OF MINERAL ORES

Our research work (2,3,14,15) as well as a literature review reveal that cobalt and molybdenum are eminently suited catalysts for hydrogenation and hydrodesulfurization of coal, whereas nickel and molybdenum are good for hydrodenitrogenation. Other metals like iron, copper, tin, zinc, platinum, and tungsten have also been found to be effective in coal liquefaction (16). Further, it has also been demonstrated that the mineral matter in coal acts as a catalyst in coal liquefaction (4). The most inexpensive source of these metals is their ores where they are present mostly as sulfides or oxides.

Cobalt is usually recovered as a by-product in the mining of copper, nickel, and silver ores, and in some localities as a by-product of iron, chromium, lead, zinc, uranium, or manganese. The copper ores of Zaire and Zambia, Africa contain as high as three to four percent of cobalt. The ores of Sudbury district of Ontario, Canada have a cobalt content of 0.07%. The small modules on the ocean floor contain 1.6% nickel and 0.21% of cobalt along with manganese, copper, and other metals. The presence of arsenic in some of the ores of cobalt should not be considered as a drawback since it is reported that arsenic assists coal liquefaction (16).

About 66% of molybdenum is produced mainly from the ore molybdenite (MoS_2). The remainder is obtained as a by-product of copper from copper minerals by selective flotation, and from tungsten and uranium ores.

Nickel occurs as nickel-copper sulfides, nickel silicates, or laterites. Pentlandite, $(\text{NiFe})_9\text{S}_8$ occurs in association with chalcopyrites (CuFeS_2). It is also available as a by-product in copper production.

MATERIAL, APPARATUS AND EXPERIMENTAL PROCEDURE

The major materials used in this study consisted of bituminous coal, SRC distillate and disposable ore catalysts. The hydrogenation reaction was carried out in an internally stirred autoclave. Hydrogen gas at high pressure was supplied to the autoclave by a compressor.

Bituminous coal from Blacksville mine, Pittsburgh Bed was used in this study. Proximate and ultimate analyses of the coal are presented in Table I. The vehicle oil used was SRC-II heavy distillate.

The hydrogenating catalyst ores were obtained from mining companies. The details of these ores are presented in Table II. The operating variables are shown in Table III.

Table III
Operating Variables for Coal Liquefaction Using
Disposable Catalysts

Coal	Blacksville Mine #2 Pittsburgh Bed #8
Solvent	SRC-II (232 - 454°C)
Gas	Hydrogen
Temperature	425°C
Pressure	~ 2000 psig (13,790 kPa)
Time of Reaction	30 minutes

Apparatus

The hydrogenation reaction was carried out in a stainless steel liner placed in a high pressure internally stirred autoclave of one liter capacity. The experiments were carried out at the stirrer speed of 1500 rpm. The autoclave was provided with a cooling coil through which water could be passed to reduce the reaction temperature if so desired. The autoclave had an electric furnace around the vessel to heat it. The temperature was controlled by a proportional temperature controller. The temperature of the reaction mass was continuously monitored by a temperature recorder. In addition, the autoclave was provided with a thermowell, a pressure gauge, a vent, a sampling valve and a safety rupture disc. A compressor was used to pressurize the autoclave.

TABLE I

Proximate and Ultimate Analyses of Coal Sample

Proximate Analysis

	As Recd.	Moist. Free	Moist., Ash Free
	%	%	%
Moisture	1.2	N/A	N/A
Volatile	35.8	36.2	41.0
Fixed Carbon	51.5	52.1	59.0
Ash	11.5	11.7	N/A

Ultimate Analysis

	As Recd.	Moist. Free	Moist., Ash Free
	%	%	%
Hydrogen	5.0	4.9	5.5
Carbon	72.0	72.9	82.5
Nitrogen	1.0	1.2	1.4
Sulfur	2.7	2.7	3.1
Oxygen	7.7	6.7	7.6
Ash	11.5	11.7	N/A
Btu/lbm	12,892	13,052	14,776

TABLE II
Analyses of Catalysts Used
(Major Constituents)

		%
Limonite	Si	16.4
	Fe	20.2
	Cr	0.5
	Ni	2.2
	Mg	9.8
	Al	1.4
Falconbridge nickel ore lumps (FNOL)	Al	2.0
	Ca	2.7
	Cu	1.0
	Fe	39.6
	Mg	0.9
	Ni	3.2
	S	15.3
	Si	5.9
Molybdenum Oxide concentrate	Mo	55.9
	Al	0.5
	Ca	0.5
	Cu	0.5
	Fe	3.6
	Mg	0.6
	Si	3.2
Molybdenum sulfide concentrate	Mo	49.8
	Si	2.6
	S	23.5
	Fe	0.7
	Ca	0.6
	FeS ₂	80.0
Iron pyrites	FeS ₂	80.0
	Al	5.2
	Ca	1.9
	Fe	2.5
	K	3.9
	Si	27.0
	Mg	0.8
Rare earth	S	0.6
	Si	2.1
	Co	1.9
	Mo	8.6
	Al	37.4
Harshaw Co-Mo (0402T)	Cr	7.6
	Al	0.8
	Fe	2.4
	K	0.6
	Mg	1.7
	Mo	0.5
	S	0.5
	Si	5.3
Bastnasite	Cr	7.6
	Al	0.8
	Fe	2.4
	K	0.6
	Mg	1.7
	Mo	0.5
	S	0.5

Experimental Procedure

Each of the experimental runs consisted of two cycles. In the first cycle, SRC-II oil was used as the vehicle oil while in the second cycle, the product oil from the first cycle was used instead. This procedure was followed so that the experimentation was done under similar conditions as would exist in a commercial-scale operation, where a part of the coal-derived oil would be recycled as the vehicle oil. The results of this study, thus, would be more useful in the commercialization of this technology. Since the percent of coal-derived oil was higher in the product oil obtained in the second cycle than in the first, the effect of the catalyst would be better reflected in the second rather than in the first cycle of liquefaction.

First Cycle Liquefaction: Coal as received was crushed and pulverized in a micromil to pass through 200 mesh screen. Forty grams of this crushed coal was taken in the liner. About 83.6 gms of SRC-II oil (in approximately 1:2.1 ratio) was then added to the liner. Pre-determined amount of the catalyst or a ore, of -200 mesh size, was next added to the contents of the liner. The stirrer assembly was fitted onto the autoclave and securely bolted. After making sure that there was no leakage, the autoclave was purged with hydrogen three or four times to drive out any air and keep the contents of the liner in a total hydrogen atmosphere. The autoclave was then pressured to a pre-determined value depending upon the room temperature, so that a pressure of about 2000 psig (13.79 MPa) was reached at 797°F (425°C) reaction temperature. The heating was initiated thereafter. Throughout this study, the experimental parameters were set at the SRC-II pilot plant operating conditions as presented in Table III. It usually took 65-70 minutes to heat the autoclave and its contents from room temperature to 797°F (425°C). The reaction was then allowed to proceed for 30 minutes. The temperature was maintained at 797°F (425°C) during this period by controlling the furnace temperature. After 30 minutes, the reaction was arrested by turning off the power to the furnace and cooling the contents down rapidly by passing cold water through the cooling coil. The autoclave was allowed to cool down to the room temperature by leaving it overnight. The liquefied products were then taken out of the autoclave and hot filtered (17) to remove unconverted coal, ash and catalyst. The filtered oil and residue were weighted and percent conversion and liquefaction calculated. Viscosity of the product oil was determined using a Brookfield Viscometer.

Second Cycle Liquefaction: The same procedure was repeated using product oil from the first cycle as the vehicle oil in place of SRC-II oil.

DISCUSSION OF RESULTS

The main objective of this investigation was to study the effects of ores and ore concentrates containing primarily cobalt, molybdenum, and nickel, as disposable catalysts in coal liquefaction. Experiments were also conducted using a commercial catalyst (Harshaw Chemicals, 0402T) and no catalyst at all to compare the results. Since iron pyrite has been reported to be a good disposable catalyst, experiments were also conducted using pyrite individually as well as in admixture with a nickel ore. The chemical analyses of the mineral ores, concentrates, and commercial catalyst are presented in Table II. The percent conversion, percent oil yield, and viscosity, of the product oils are presented in Table IV.

Percent conversion and liquefaction of coal are defined as follows:

$$\text{Percent Conversion} = \frac{(\text{Original Cost (macf)} - \text{Toluene Insolubles (macf)}) \times 100}{\text{Original Coal (macf)}}$$

TABLE IV

Effect of Catalyst on Liquefaction of Coal

Temperature Reaction Time Wt. of Coal		797 F (425 C) : 30 minutes : 40.0 gms	Pressure Stirrer speed		2000 psig (13.79 MPa) : 1500 rpm		
SN	Cycle Catalyst used	% Catalyst based on Coal(maf)	Coal: Vehicle Oil	Conversion	Liquefaction	Product Oil Viscosity, cp at 60 C	Conversion minus Liquefaction
1	I	-----	2.10	83.96	70.73	20.8	13.23
2	II	-----	2.10	60.20	43.24	81.0	16.96
3	I Co-Mo	2.49	2.09	84.45	74.17	17.9	10.28
4	II Co-Mo	2.55	2.09	80.50	68.16	57.4	12.34
5	I Co-Mo	5.04	2.10	80.13	69.30	15.6	10.83
6	II Co-Mo	5.05	2.09	76.13	63.57	47.0	12.56
7	I MoO Conc.	2.48	2.09	82.72	75.60	23.4	7.12
8	II MoO Conc.	2.59	2.09	76.82	63.00	56.2	13.82
9	I MoS Conc.	2.51	2.09	83.61	73.31	23.9	10.30
10	II MoS Conc.	2.51	2.10	70.15	59.57	62.6	10.58
11	I Limonite	2.49	2.13	83.02	73.31	21.6	9.71
12	II Limonite	2.50	2.09	70.43	58.71	66.0	11.72
13	I Rare Earth	2.51	2.09	87.33	75.60	20.3	11.73
14	II Rare Earth	2.52	2.10	70.16	56.42	74.2	13.74
15	I Bastnaesite	2.52	2.19	83.33	71.31	19.3	12.02
16	II Bastnaesite	2.51	2.10	75.30	57.85	75.0	17.45
17	I FNOL	2.51	2.09	88.76	73.02	22.4	15.74
18	II FNOL	2.52	2.10	73.02	54.12	74.2	18.90
19	I Iron Pyrite	2.52	2.14	83.37	71.59	18.4	12.32
20	II Iron Pyrite	2.53	2.10	71.64	59.28	60.4	12.90
21	I Iron Pyrite	2.51	2.30	85.58	72.45	19.7	13.66
22	II Iron Pyrite	2.58	2.33	80.19	68.19	54.8	12.58
	Limonite	2.51					

Percent Liquefaction = Oil Products x 100/Original Coal (macf)
where macf = moisture, ash, catalyst free.

Effect of Mineral Ores

Liquefaction of coal was conducted using molybdenum sulfide concentrate, molybdenum oxide concentrate, Falconbridge nickel ore lumps (FNOL), bastnasite, rare earth ore, limonite, and iron pyrite. Table IV lists the results of these experiments.

As can be seen, increasing the concentration of the commercial Co-Mo catalyst from 2.5% to 5.0% based on coal (maf), did not bring about any significant change in the percent conversion, liquefaction, or the product oil viscosity. Hence, experiments with all the mineral ores were conducted at 2.5% concentration.

The results of the first cycle liquefaction, namely, the percent conversion, liquefaction, and the product oil viscosity did not show any appreciable change with the catalysts used. As was discussed earlier, the product oil from the first cycle liquefaction contained only 15% coal-derived oil, and therefore, did not cause any appreciable change in the overall viscosity of the product oil.

On the contrary, since there was about 30% coal-derived oil in the second cycle product oil, the amount and viscosity of the former had a greater effect on the overall viscosity of the product oil. Therefore, the catalytic effect of these mineral ores were better reflected in the results of the second cycle liquefaction than in the first.

Referring to Table IV, it was also seen that the percent conversion and liquefaction and the viscosity of the product oil in the second cycle of liquefaction obtained using the mineral ores were much better than those obtained using no catalyst. The percent conversion using these mineral ores was in the range of 70-80% as against 60% without any catalyst. The percent liquefaction was in the range of 54-68% as compared to 43% obtained without any catalyst. The product oil viscosity also showed a marked improvement.

Molybdenum oxide concentrate, when used as a catalyst, gave 76.82% conversion and 63.00% liquefaction, which compares well with 80.50% conversion and 68.16% liquefaction obtained using 2.5% commercial Co-Mo catalyst. However, the viscosity of the product oil was 66.2 cp as compared to 57.4 cp obtained using the commercial Co-Mo catalyst. Therefore, the performance of molybdenum oxide concentrate as a catalyst in coal liquefaction was found to be only slightly lower than that of the commercial Co-Mo catalyst. The lower cost of molybdenum oxide concentrate as compared to the commercial Co-Mo catalyst, should more than compensate for its lower catalytic activity.

The 70.15% conversion and 59.57% liquefaction obtained using molybdenum sulfide concentrate as catalyst were lower than that obtained using molybdenum oxide concentrate. However the viscosity of the product oil was 60.3 cp as against 66.2 cp that molybdenum oxide concentrate yielded. The decrease in the percent liquefaction could have resulted in a decrease in the viscosity of the product oil.

Rare earth, bastnasite, limonite, and Falconbridge nickel ore lumps (FNOL) gave percent conversion and liquefaction ranging from 70-75% and 54-58%, respectively. The viscosity of the product oils obtained ranged from 66-75 cp, indicating that the quality of the product oil was inferior to that obtained using molybdenum oxide and molybdenum sulfide concentrates. The difference between the percent conversion and liquefaction (vide, Table IV) also showed that bastnasite and FNOL converted more of the coal to gas than the other mineral ores tested in this study.

Hence, it could be inferred that these mineral ores at 2.5% concentration exhibited less catalytic activity for coal liquefaction.

Iron Pyrite, a by-product of coal-mining operation gave 71.64% conversion and 59.28% liquefaction. Also, it yielded a product oil of viscosity 60.4 cp which was lower than that obtained using molybdenum oxide concentrate. This lower viscosity in the case of iron pyrite could be due to less coal-derived oil produced because of the lower percent liquefaction achieved. Also, the conversion and liquefaction obtained using iron pyrite were lower than the 80.50% conversion and 68.15% liquefaction achieved using the commercial Co-Mo catalyst. Iron pyrite yielded a product oil viscosity of 60.4 cp as compared to 57.4 cp obtained using the commercial Co-Mo catalyst.

Effect of Mixture of Mineral Ores on Liquefaction

Addition of limonite to the iron pyrite was found to considerably improve the liquefaction obtained using the pyrite alone. A 1:1 mixture of iron pyrite and limonite increased the percent conversion and liquefaction to 80.74% and 68.16%, respectively, as compared to 71.64% and 59.28% obtained using the pyrite alone. The viscosity of the product oil improved to 54.8 cp from 60.4 cp. Thus, a mixture of iron pyrite and limonite worked equally well, if not better, as the commercial Co-Mo catalyst in the coal liquefaction process.

CONCLUSIONS

The results of this study showed that ores containing metals such as cobalt, molybdenum, and nickel were catalytically active for the liquefaction of coal; the molybdenum oxide showed the best results. The reactivity of iron pyrite was found to increase when used in admixture with limonite. This increase in activity is specially noteworthy since iron pyrite is available in large amount, and at present is considered to be the best available disposable catalyst.

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REFERENCES

1. Katell, S., L.G. White, "Clean Fuels from Coal are Expensive," Hydrocarbon Processing, 8, 83, 1976.
2. O'Leary, M.J., D.C. Stetson, V.K. Mathur, "Catalytic Liquefaction of Coal," Coal Processing Technology, Vol. V., 1979.
3. Mathur, V.K., "Coal Power, Its Promises and Problems," A series of energy sources, their promises and problems, published by the Center for Industrial and Institutional Development, University of New Hampshire, Durham, NH, Feb. 1980.
4. Calderwood, W., "Catalytic Hydrodenitrogenation of Coal Using CO-Steam and Hydrogen," Internal Report, Department of Chemical Engineering, University of New Hampshire, 1979.

5. Thakkau, V.P., "Kinetics of the Hydrodenitrogenation of Nitrogen Compounds in a Coal-Derived Oil," Ph.D. Thesis, Colorado School of Mines, 1978.
6. Smith, W.M., T.C. Landron, G.E. Phillips, "Hydrogenation of Shale Oil," Ind. Eng. Chem., 44, 586, 1952.
7. Staubs, D.W., R.L. Miller, H.F. Silver, R.J. Hurtubise, "The Effect of Solvent Refined Coal Denitrification," Ind. Eng. Chem. Proc. Design and Dev., Vol. 18, 4,667,1979.
8. Satterfield, C.N., M. Modell, R.A. Hites, C.J. Declerck, "Intermediate Reaction in the Catalytic Hydrodenitrogenation of Quinoline," Ind. Eng. Chem. Proc. Design and Dev., 17, 141, 1978.
9. Cusumano, J.A., R.A. Dalla Betta, R.B. Levy, "Catalysis in Coal Conversion," Academic Press, 1978.
10. Jackson, D.M., B.K. Schmid, "Commercial Scale Development of the SRC-II Process," Presented at the Fifth Annual International Conference on Commercialization of Coal Gasification, Liquefaction and Conversion to Electricity, University of Pittsburgh, PA, Aug. 1978.
11. Ellington, R.T., Liquid Fuels from Coal, Academic Press, New York, p. 45, 1977.
12. Mineral Facts and Problems, Bureau of Mines Bulletin No. 667, U.S. Department of the Interior, 1976.
13. Brobst, D.A., W.P. Pratt (ed.), U.S. Mineral Resources Geological Survey Professional Paper 820, U.S. Department of Interior, 1973.
14. Stetson, D.C., "Catalytic Liquefaction of Coal Using Carbon Monoxide and Steam," M.S. Thesis, University of New Hampshire, 1977.
15. Guttal, V., "Catalytic Desulfurization of Coal Using CO and Steam," M.S. Thesis, University of New Hampshire, 1979.
16. Weller, S., M.G. Pelepetz, S. Frierman, H.H., Storch, "Coal, Hydrogenation Catalysts," Ind. Eng. Chem., Vol. 42,2,330, 1950.
17. Venkataramanan, V., "Liquefaction of Coal Using Disposable Catalysts," M.S. Thesis, University of New Hampshire, 1981.